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(54) **Crucible for master alloying**

Tiegel für Masterlegierung

Creuset pour alliage mère

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(56) References cited:
EP-A1- 1 990 593 DE-T2- 69 416 762
JP-A- 1 083 569 JP-A- 3 223 414
JP-A- 63 014 080 US-A- 4 006 891

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Description

BACKGROUND

[0001] This disclosure relates to crucibles and crucible linings, used for the manufacturing of master alloys, which are e.g. described in US 4,006,891 A.

[0002] Superalloy ingot materials for casting processes are typically fabricated in a master alloying process. The process involves placing virgin elements, revert alloy, or any combination thereof of materials that comprise the alloy into a crucible. These materials are then subsequently heated in such a manner to produce a homogeneous molten alloy with the desired composition. Impurities may also be removed during the process, through chemical or physical means such as by desulphurization and commercially available molten metal filters. After establishing homogeneity, the molten alloy is then transferred from the crucible into an ingot tube. In some cases a tundish is employed to control the distribution of molten metal in to the ingot tubes. The solidified ingot is then subsequently processed for use at the casting furnace. The process can also be used to directly cast the master melted alloy chemistry directly into an investment cast, permanent mold, or other suitable vessel to contain the molten metal.

SUMMARY

[0003] An example crucible includes a composite of at least two materials. The two materials are selected from a group consisting of alumina, calcia, yttria, erbia, gadolinia, magnesia, hafnia, and zirconia. Disclosed is a composition that has better resistance to reaction with hafnium from a molten hafnium-containing alloy than a nominal crucible composition of 70wt% magnesia and 30wt% alumina.

BRIEF DESCRIPTION OF THE DRAWINGS

[0004] The various features and advantages of the disclosed examples will become apparent to those skilled in the art from the following detailed description. The drawings that accompany the detailed description can be briefly described as follows.

Figure 1 illustrates an example ceramic crucible that includes a composite material of a composition having good resistance to reaction with hafnium.

Figure 2 illustrates an example refractory brick lined crucible that includes a composite material of a composition having good resistance to reaction with hafnium.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0005] Figures 1 and 2 illustrate selected portions of

example vessels 20 and 20' that may be used for master alloying processes, such as to mix alloy compositions and/or remove impurity elements (e.g., desulfurization). As will be described, the vessels 20 and 20' have better resistance to reaction with hafnium from a molten hafnium-containing alloy than a standard ceramic crucible having a nominal composition of approximately 70wt% magnesia and 30wt% alumina.

[0006] The alloy may be a nickel-based superalloy and the hafnium may be present in an amount of approximately 0.1-10 wt%, but most commonly is present in an amount of 0.1-2wt%. Hafnium (hafnium metal, hafnia, or both) from a batch of molten hafnium-containing alloy may leach into a standard crucible or crucible lining and react with the crucible material. During subsequent processing of another batch of non-hafnium alloy in the standard crucible, the hafnium may leach out of the crucible material and into the subsequent batch to thereby alter or contaminate the composition of the subsequent batch rendering it out of specification. In this regard, the exemplary vessels 20 and 20' include a composite material in a composition that has better resistance to chemically reacting with hafnium than the standard crucible such that poisoning of the subsequent batches through the reaction and leaching of hafnium is reduced or even substantially eliminated, as detected through known techniques for determining alloy composition. Additionally, the exemplary vessels 20 and 20' may be used in combination with other techniques, such as "late addition" charging of hafnium into the vessels 20 and 20', to reduce the overall reaction time at temperature reducing the reaction and leaching of hafnium. For instance, the hafnium may be added to the molten alloy is not at the processing temperature (e.g., 2500-2750°F or 1371-1510°C) for more than thirty minutes after the addition of the element. The vessels 20 and 20' also is not subject to a high rate of degradation from the reactions with hafnium.

[0007] In Figure 1, the vessel 20 includes a crucible 22 that has an interior space 24 for holding the raw materials for making an alloy and the molten alloy. In general, the crucible 22 is shaped like a cup or ladle. However, the crucible 22 may be designed with other geometries and components, such as heating/cooling mechanisms, to suit the particular needs of an application.

[0008] The crucible 22 includes an exterior surface 26a and an interior surface 26b with regard to the interior space 24 where the alloy is processed. In the example, the crucible 22 includes a liner 28 that is located adjacent to the interior surface 26b. Induction coils 30 generally surround the crucible 22 to heat the interior space 24. The liner 28 is made of the composite material that is resistant to reaction with hafnium. The liner 28 may be a coating or layer that is applied onto the crucible 22. For instance, the crucible 22 may include a non-reactive refractory material, such as alumina, magnesia, combinations thereof, or other material that has a different composition from the composite material of the liner 28, and

that serves as a substrate for the liner 28. The refractory material may be a solid, monolithic wall in the form of the crucible 22 or refractory bricks that are assembled into the shape of the crucible 22', as shown in the modified vessel 20' of Figure 2 for example. The liner 28 may be applied onto the crucible 22 using known coating or powder processing techniques, such as slurry spray processing.

[0009] Alternatively, the crucible 22 may be a monolithic article that does not include the liner 28 but instead is made of the composite material that is resistant to reaction with hafnium. A user may manufacture the crucible 22 using known processing techniques, such as slip casting, dry pressing, or isostatic pressing.

[0010] The composite material according to independent claim 1, that is resistant to reaction with hafnium includes at least two materials from the group containing: alumina (Al₂O₃), calcia (CaO), yttria (Y₂O₃), erbia (Er₂O₃), gadolinia (Gd₂O₃), magnesia (MgO), hafnia (Hf₂O), and zirconia (Zr₂O₃) in a composition. This material has better resistance to reaction with hafnium from a molten hafnium-containing alloy than a nominal crucible composition of approximately 70wt% magnesia and 30wt% alumina. In some examples, the composite material includes at least three or at least four of the materials to provide the resistance to reaction with hafnium.

[0011] A few examples of ternary composite materials, which are not part of the invention, include calcia/magnesia/alumina, yttria/magnesia/alumina, yttria/calcia/alumina, yttria/zirconia and one of alumina, calcia, or magnesia, and any two of the above-listed materials and hafnia.

[0012] A few examples of quaternary composite materials include yttria/gadolinia/zirconia and one of alumina, calcia, or magnesia, and any three of the above-listed material and hafnia.

[0013] As an example, the materials of the composite are selected based on stability with regard to the free energy of reaction (e.g., Ellingham diagram for oxide formation). In that regard, hafnium metal would be expected to react with relatively low-stability oxides of a crucible to preferentially form hafnium oxide. However, if at least a portion of the composite material is composed of a highly stable material, the crucible becomes more resistant to reaction with the hafnium. Yttria and calcia are examples of highly stable oxides that reduce the tendency of hafnium metal to react and form hafnium oxide.

[0014] The following examples illustrate additional compositions.

Binary Composite Materials

[0015] The composite material may be a binary composite that includes yttria, and the yttria may be present in an amount greater than 10wt%. In one example, the composite material includes greater than 10wt% yttria and a balance of alumina.

[0016] A composite, which is not part of the invention,

is a binary composite of calcia and alumina, and the calcia is present in an amount greater than 65wt%.

[0017] In another alternative, the composite material may be yttria stabilized zirconia ("YSZ"), and the yttria may be present in an amount of 6-9wt%.

[0018] In another example, the composite material is a binary composite of any of the listed materials and hafnia, and the hafnia may be present in an amount of at least 10wt%. The presence of hafnia in the composite material reduces the concentration gradient of hafnium between the composite material and the hafnium-containing alloy such that there is a reduction of diffusion of hafnium metal into the composite material for reaction.

Ternary Composite Materials

[0019] The composite material may be a ternary composite. For example, the composite material may include three materials of calcia, yttria, magnesia, and alumina. For instance, the composite material includes yttria, magnesia and alumina such that the composite material, which is not part of the invention, includes less than 20wt% yttria, less than 20wt% magnesia, and a balance of alumina. The composite material may alternatively be alumina, yttria, and calcia such that the composite material includes less than 20wt% yttria, less than 20wt% calcia, and a balance of alumina. Alternatively, the composite material is calcia, magnesia, and alumina such that the composite material includes less than 20wt% calcia, less than 20wt% magnesia, and a balance of alumina.

[0020] In another example, the composite material may include yttria, zirconia, and at least one of alumina, calcia, or magnesia. For instance, the yttria may be present in an amount of 6-9wt% based on the combined weight of the yttria and zirconia.

Quaternary Composite Materials

[0021] The composite material may be a quaternary composite. For example, the composite material may include yttria, zirconia, and gadolinia with any of alumina, calcia, hafnia, or magnesia.

[0022] Additionally, in any of the above binary, ternary, or quaternary examples that include yttria, the elements gadolinia, zirconia, or both may be used with the yttria or even substituted for the yttria. For instance, the combined amount of yttria, gadolinia, and zirconia is greater than 10wt%.

[0023] Although a combination of features is shown in the illustrated examples, not all of them need to be combined to realize the benefits of various embodiments of this disclosure. In other words, a system designed according to an embodiment of this disclosure will not necessarily include all of the features shown in any one of the Figures or all of the portions schematically shown in the Figures. Moreover, selected features of one example embodiment may be combined with selected features of

other example embodiments.

[0024] In an alternative embodiment, the invention is directed to a vessel for master alloying, the vessel comprising:

a crucible including a liner that is made of a composite of at least two materials selected from a group consisting of alumina, calcia, yttria, erbia, gadolinia, magnesia, hafnia, and zirconia.

[0025] The preceding description is exemplary rather than limiting in nature. Variations and modifications to the disclosed examples may become apparent to those skilled in the art that do not necessarily depart from the essence of this disclosure. The scope of legal protection given to this disclosure can only be determined by studying the following claims.

Claims

1. A vessel for master alloying, the vessel comprising: a crucible including a composite of at least two materials selected from a group consisting of alumina, calcia, yttria, erbia, gadolinia, magnesia, hafnia, and zirconia in a composition that has better resistance to reaction with hafnium from a molten hafnium-containing alloy than a nominal crucible composition of 70wt% magnesia and 30wt% alumina; wherein the composite is selected from the following: a binary composite of yttria and alumina which includes greater than 10wt% of yttria; a binary composite of yttria and zirconia which includes 6-9wt% of yttria; a ternary composite of yttria, zirconia and one of alumina and magnesia which includes 6-9wt% of yttria.
2. The vessel as recited in claim 1, wherein the composite is the binary composite of alumina and yttria which includes greater than 10wt% yttria.
3. The vessel as recited in claim 1, wherein the composite is the binary composite of yttria and zirconia which includes 6-9wt% of yttria.
4. The vessel as recited in claim 1, wherein the composite is the ternary composite of yttria, zirconia and one of alumina and magnesia which includes 6-9wt% yttria.
5. The vessel as recited in any of claims 1 to 4, wherein the crucible includes a liner that is formed of the composite.

Patentansprüche

1. Gefäß für Masterlegierung, wobei das Gefäß Folgendes umfasst: einen Tiegel, beinhaltend einen Verbundstoff, bestehend aus mindestens zwei Materialien, ausgewählt

aus einer Gruppe bestehend aus Aluminiumoxid, Calciumoxid, Yttriumoxid, Erbiumoxid, Gadoliniumoxid, Magnesiumoxid, Hafnium und Zirkonoxid in einer Zusammensetzung, die widerstandsfähiger gegenüber der Reaktion mit Hafnium aus einer geschmolzenen, Hafnium beinhaltenden Legierung ist als eine nominale Tiegelzusammensetzung bestehend aus 70 Gew.-% Magnesiumoxid und 30 Gew.-% Aluminiumoxid; wobei der Verbundstoff aus den Folgenden ausgewählt ist: ein binärer Verbundstoff aus Yttriumoxid und Aluminiumoxid, der mehr als 10 Gew.-% Yttriumoxid enthält; ein binärer Verbundstoff aus Yttriumoxid und Zirkonoxid, der 6-9 Gew.-% Yttriumoxid enthält; ein ternärer Verbundstoff aus Yttriumoxid, Zirkonoxid und einem von Aluminiumoxid und Magnesiumoxid, der 6-9 Gew.-% Yttriumoxid enthält.

2. Gefäß nach Anspruch 1, wobei der Verbundstoff der binäre Verbundstoff aus Aluminiumoxid und Yttriumoxid ist, der mehr als 10 Gew.-% Yttriumoxid enthält.
3. Gefäß nach Anspruch 1, wobei der Verbundstoff der binäre Verbundstoff aus Yttriumoxid und Zirkonoxid ist, der 6-9 Gew.-% Yttriumoxid enthält.
4. Gefäß nach Anspruch 1, wobei der Verbundstoff der ternäre Verbundstoff aus Yttriumoxid, Zirkonoxid und einem von Aluminiumoxid und Magnesiumoxid ist, der zwischen 6-9 Gew.-% Yttriumoxid enthält.
5. Gefäß nach einem der Ansprüche 1 bis 4, wobei der Tiegel eine aus dem Verbundstoff gebildete Auskleidung beinhaltet.

Revendications

1. Récipient pour alliage mère, le récipient comprenant : un creuset comportant un composite d'au moins deux matériaux sélectionnés parmi un groupe comprenant l'oxyde d'aluminium, l'oxyde de calcium, l'oxyde d'yttrium, l'oxyde d'erbium, l'oxyde de gadolinium, l'oxyde de magnésium, l'oxyde d'hafnium et l'oxyde de zirconium dans une composition qui a une meilleure résistance à la réaction avec le hafnium à partir d'un alliage contenant du hafnium fondu par rapport à une composition de creuset nominale de 70 % en poids d'oxyde de magnésium et de 30 % en poids d'oxyde d'aluminium ; dans lequel le composite est sélectionné parmi les éléments suivants : un composite binaire d'oxyde d'yttrium et d'oxyde d'aluminium qui comporte plus de 10 % en poids d'oxyde d'yttrium ; un composite binaire d'oxyde d'yttrium et d'oxyde de zirconium qui comporte de 6 à 9 % en poids d'oxyde d'yttrium ; un composite ternaire d'oxyde d'yttrium, d'oxyde de zirconium et de

l'un de l'oxyde d'aluminium et de l'oxyde de magnésium qui comporte de 6 à 9 % en poids d'oxyde d'yttrium.

2. Récipient selon la revendication 1, dans lequel le composite est le composite binaire d'oxyde d'aluminium et d'oxyde d'yttrium qui comporte plus de 10 % en poids d'oxyde d'yttrium. 5
3. Récipient selon la revendication 1, dans lequel le composite est le composite binaire d'oxyde d'yttrium et d'oxyde de zirconium qui comporte de 6 à 9 % en poids d'oxyde d'yttrium. 10
4. Récipient selon la revendication 1, dans lequel le composite est le composite ternaire d'oxyde d'yttrium, d'oxyde de zirconium et de l'un de l'oxyde d'aluminium et de l'oxyde de magnésium qui comporte de 6 à 9 % en poids d'oxyde d'yttrium. 15
5. Récipient selon l'une quelconque des revendication 1 à 4, dans lequel le creuset comporte un revêtement qui est constitué du composite. 20

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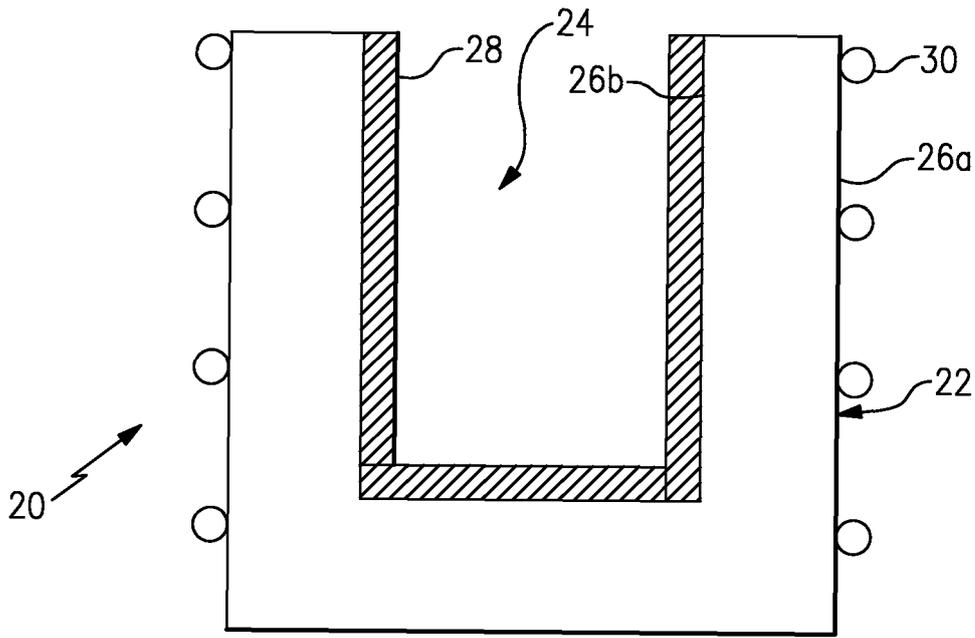


FIG. 1

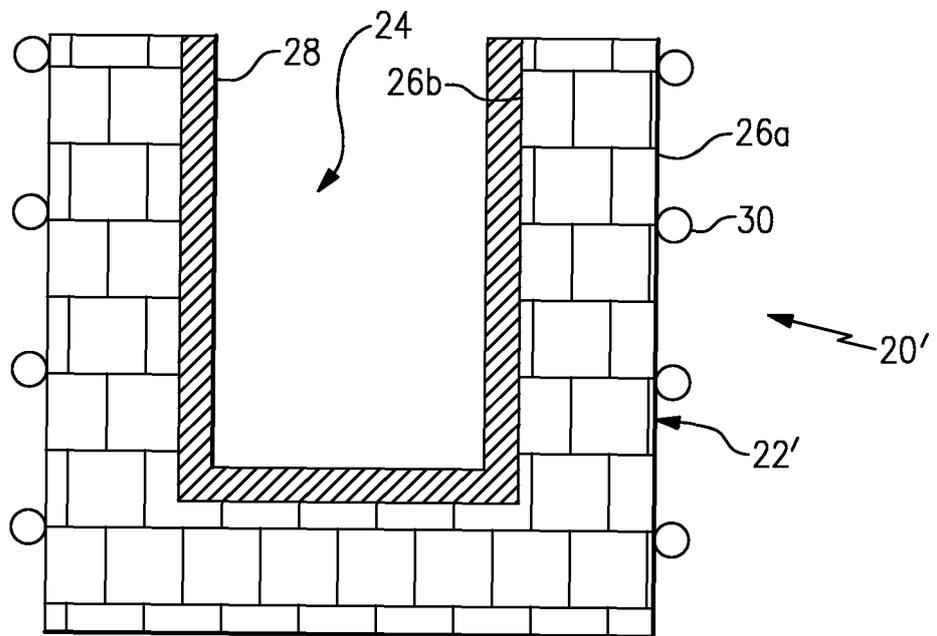


FIG. 2

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 4006891 A [0001]